CLAIMS

1. A process for forming a lubricative film for cold working on a metal substrate, said process comprising the following operations:

(I) bringing said metal substrate into contact with an aqueous electrolyte solution comprising water and:

(A) dissolved zinc cations;

(B) dissolved phosphate anions; and

(C) at least one dissolved auxiliary acid other than phosphoric acid, said auxiliary acid having at least a first ionization constant that is greater than the third ionization constant for phosphoric acid; and, optionally, other constituents as detailed further below,

this aqueous electrolyte also being in contact with a counter-electrode that is not said metal substrate to be cold worked, so that an electric current can pass through the counter-electrode as anode, the aqueous electrolyte solution by ionic conduction, and said metal substrate as cathode;

(II) passing through said metal substrate while it remains in contact with said aqueous electrolyte solution an electric current that has a net cathodizing character at said metal substrate for a sufficient time to form an adherent solid phosphate conversion coating over said metal substrate;

(III) discontinuing contact between said aqueous electrolyte solution and said metal substrate bearing said adherent solid phosphate conversion coating; and

(IV) applying to the exterior surface of said solid phosphate conversion coating, when it is not in contact with said aqueous electrolyte solution, a water- or oil-based lubricant coating.

2. A process according to claim 1, wherein said aqueous electrolyte solution in operation (I):

- comprises at least 20 g/l of dissolved zinc cations and at least 20 g/l of dissolved phosphate anions; and
- has a pH value at least as low as the pH value of a hypothetical reference electrolyte solution that contains the same actual amounts of dissolved zinc and phosphate ions as does said aqueous electrolyte solution and in addition contains at least 30 g/l of nitric acid as its only auxiliary acid.

3. A process according to claim 2, wherein said aqueous electrolyte solution additionally comprises at least one type of divalent or trivalent metal ions selected from the group consisting of magnesium, aluminum, calcium, manganese, chromium, iron, nickel,

and copper.

4. A process according to claim 3, wherein said aqueous electrolyte solution comprises a concentration of calcium ions such that the molar ratio of calcium ions to zinc ions is from 0.1:1 to 2:1.

5. A process according to claim 4, wherein before operation (I), said substrate is acid pickled and then rinsed with water.

6. A process according to claim 5, wherein after being acid pickled and rinsed with water, said substrate is brought into contact with a surface conditioning liquid containing colloidal titanium, dispersed metal phosphate particles including particles with a diameter of 5 μm or less, or both colloidal titanium and dispersed metal phosphate particles with a diameter of 5 μm or less.

7. A process according to claim 6, wherein the lubricant coating applied in operation (IV) is a water-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of dissolved alkali metal salts of fatty acids, dispersed metallic soaps, and dispersed solid lubricants.

8. A process according to claim 6, wherein the lubricant coating applied in operation (IV) is an oil-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of mineral oils, animal oils, and synthetic ester oils.

9. A process according to claim 1, wherein said aqueous electrolyte solution additionally comprises at least one type of divalent or trivalent metal ions selected from the group consisting of magnesium, aluminum, calcium, manganese, chromium, iron, nickel, and copper.

10. A process according to claim 9, wherein said aqueous electrolyte solution comprises a concentration of calcium ions such that the molar ratio of calcium ions to zinc ions is from 0.1:1 to 2:1.

11. A process according to claim 10, wherein before operation (I), said substrate is acid pickled and then rinsed with water.

12. A process according to claim 11, wherein after being acid pickled and rinsed with water, said substrate is brought into contact with a surface conditioning liquid containing colloidal titanium, dispersed metal phosphate particles including particles with a diameter of 5 μm or less, or both colloidal titanium and dispersed metal phosphate particles with a diameter of 5 μm or less.

13. A process according to claim 12, wherein the lubricant coating applied in operation (IV) is a water-based lubricant that comprises at least one type of lubricant

substance selected from the group consisting of dissolved alkali metal salts of fatty acids, dispersed metallic soaps, and dispersed solid lubricants.

14. A process according to claim 12, wherein the lubricant coating applied in operation (IV) is an oil-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of mineral oils, animal oils, and synthetic ester oils.

15. A process according to claim 1, wherein before operation (I), said substrate is acid pickled and then rinsed with water.

16. A process according to claim 15, wherein after being acid pickled and rinsed with water, said substrate is brought into contact with a surface conditioning liquid containing colloidal titanium, dispersed metal phosphate particles including particles with a diameter of 5 μm or less, or both colloidal titanium and dispersed metal phosphate particles with a diameter of 5 μm or less.

17. A process according to claim 16, wherein the lubricant coating applied in operation (IV) is a water-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of dissolved alkali metal salts of fatty acids, dispersed metallic soaps, and dispersed solid lubricants.

18. A process according to claim 16, wherein the lubricant coating applied in operation (IV) is an oil-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of mineral oils, animal oils, and synthetic ester oils.

19. A process according to claim 1, wherein before operation (I), said substrate is brought into contact with a surface conditioning liquid comprising colloidal titanium, dispersed metal phosphate particles including particles with a diameter of 5 μm or less, or both colloidal titanium and dispersed metal phosphate particles with a diameter of 5 μm or less.

20. A process according to claim 19, wherein the lubricant coating applied in operation (IV) is a water-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of dissolved alkali metal salts of fatty acids, dispersed metallic soaps, and dispersed solid lubricants.

21. A process according to claim 19, wherein the lubricant coating applied in operation (IV) is an oil-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of mineral oils, animal oils, and synthetic ester oils.